Materials and Structures

Application of Fickian and non-Fickian diffusion models to study moisture diffusion in asphalt mastics

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Corresponding Author:	Alex Apeagyei University of Nottingham Nottingham, UNITED KINGDOM
Corresponding Author Secondary Information:	
Corresponding Author's Institution:	University of Nottingham
Corresponding Author's Secondary Institution:	
First Author:	Alex Apeagyei
First Author Secondary Information:	
Order of Authors:	Alex Apeagyei
	James Grenfell
	Gordon Airey
Order of Authors Secondary Information:	
Abstract:	The objective of this study was to investigate certain aspects of asphalt mastic moisture diffusion characteristics in order to better understand the moisture damage phenomenon in asphalt mixtures. Moisture sorption experiments were conducted on four asphalt mastics using an environmental chamber capable of automatically controlling both relative humidity (85%) and temperature (23°C). The four mastics tested were identical in terms of bitumen type (40/60 pen), bitumen amount (25% by of wt total mix), mineral filler amount (25% by wt) and fine aggregate amount (50% by wt). The materials differed in terms of mineral filler type (granite or limestone) and fine aggregate type (granite or limestone). Preliminary data obtained during the early part of the study showed certain anomalous behavior of the materials including geometry (thickness)-dependent diffusion coefficient. It was therefore decided to investigate some aspects related to moisture diffusion in mastics by applying the Fickian and two non-Fickian (anomalous) diffusion models to the moisture sorption data. The two non-Fickian models included a two-phase Langmuir-type model and a two-parameter time-variable model. All three models predicted moisture diffusion in mastics extremely well ($R2 > 0.95$). The observed variation of diffusion coefficient with thickness was attributed in part to microstructural changes (settlement of the denser fine aggregates near the bottom of the material) during the rather long-duration diffusion testing. This assertion was supported by X-ray CT imaging of the mastic that showed significant accumulation of aggregate particles near the bottom of the sample with time. The results from the Langmuir-type model support a two-phase (free and bound) model for moisture absorbed by asphalt mastic and suggests about 80% of absorbed water in the free phase remain bound within the mastic. The results also suggest that moisture diffusion in asphalt mastic may be time-dependent with diffusion decreasing by about four times during a typical diffusion test lasting up to 500 hours. The study concludes that both geometry and time-dependent physical characteristics of mastic are important factors to consider with respect to moisture diffusion in asphalt mastics.

Application of Fickian and non-Fickian diffusion models to study moisture diffusion in asphalt mastics

Alex K. Apeagyei, James R. A. Grenfell & Gordon D. Airey[3]

[1]*Research Fellow, Nottingham Transportation Engineering Centre, Department of Civil Engineering, University of Nottingham, University Park, Nottingham NG7 2RD, United Kingdom; email: alex.apeagyei@nottingham.ac.uk*

[2]*Research Officer, Nottingham Transportation Engineering Centre, Department of Civil Engineering, University of Nottingham, University Park, Nottingham NG7 2RD, United Kingdom; email: james.grenfell@nottingham.ac.uk*

[3]*Professor, Nottingham Transportation Engineering Centre, Department of Civil Engineering, University of Nottingham, University Park, Nottingham NG7 2RD, United Kingdom; email: gordon.airey@nottingham.ac.uk*

Abstract: The objective of this study was to investigate certain aspects of asphalt mastic moisture diffusion characteristics in order to better understand the moisture damage phenomenon in asphalt mixtures. Moisture sorption experiments were conducted on four asphalt mastics using an environmental chamber capable of automatically controlling both relative humidity (85%) and temperature (23°C). The four mastics tested were identical in terms of bitumen type (40/60 pen), bitumen amount (25% by of wt total mix), mineral filler amount (25% by wt) and fine aggregate amount (50% by wt). The materials differed in terms of mineral filler type (granite or limestone) and fine aggregate type (granite or limestone). Preliminary data obtained during the early part of the study showed certain anomalous behavior of the materials including geometry (thickness)-dependent diffusion coefficient. It was therefore decided to investigate some aspects related to moisture diffusion in mastics by applying the Fickian and two non-Fickian (anomalous) diffusion models to the moisture sorption data. The two non-Fickian models included a two-phase Langmuir-type model and a two-parameter time-variable model. All three models predicted moisture diffusion in mastics extremely well ($R^2 > 0.95$). The observed variation of diffusion coefficient with thickness was attributed in part to microstructural changes (settlement of the denser fine aggregates near the bottom of the material) during the rather long-duration diffusion testing. This assertion was supported by X-ray CT imaging of the mastic that showed significant accumulation of aggregate particles near the bottom of the sample with time. The results from the Langmuir-type model support a two-phase (free and bound) model for moisture absorbed by asphalt mastic and suggests about 80% of absorbed water in the free phase remain bound within the mastic. The results also suggest that moisture diffusion in asphalt mastic may be time-dependent with diffusion decreasing by about four times during a typical diffusion test lasting up to 500 hours. The study concludes that both geometry and time-dependent physical characteristics of mastic are important factors to consider with respect to moisture diffusion in asphalt mastics.

Keywords: Fickian diffusion, non-Fickian diffusion, moisture diffusion, asphalt mastics, asphalt mixtures, X-ray CT

Introduction

Moisture-induced damage in asphalt mixtures is a major contributor to the development of distresses in pavements. Previous studies suggest moisture-induced damage is influenced to a greater extent by moisture diffusion characteristics of asphalt mixtures (Caro et al. 2008). Moisture diffusion coefficient is considered a key parameter that can be used to characterize moisture diffusion in hygroscopic materials such as asphalt mixtures. Moisture diffusion coefficient and other moisture diffusion characteristics of asphalt mastics (Kassem et al. 2006) and of asphalt mixtures (Sasaki et al. 2006) have all been used to demonstrate links between moisture diffusion and moisture damage in asphalt pavements in the past. Diffusion coefficient can also be used to numerically model moisture transport in asphalt pavements which is important in studying the mechanical behavior and hence performance of pavements in the presence of moisture. For instance, recently obtained experimental data have shown that moisture-induced damage in an asphalt mixture can occur due to the adverse effects of moisture on the mechanical characteristics of the mastic and / or the bond between the mastic and aggregates (Kringos et al. 2007; Kringos et al., 2008a). As a results of these studies, a finite element subsystem RoAM (Raveling of Asphalt Mixtures) within the CAPA 3-D FE system has been developed that can estimate the combined mechanical and moisture–induced damage of asphalt mixtures by simulating the physical damage due to water flow and moisture diffusion through asphaltic mixes (Kringos et al., 2008a, Kringos et al., 2008b, Kringos et al., 2008c). A key input parameter for these FE systems is the diffusion coefficient of the asphalt mixture components (mastic and aggregate).

In recognition of the importance of diffusion coefficient as a parameter for demonstrating the link between moisture diffusion and moisture damage and also diffusion coefficient and moisture damage simulations in asphalt mixtures, many recent studies have focused on experimental determination of the parameter (Table 1). The reported diffusion coefficient from these studies, however, shows great disparities as indicated by the very large range in the reported values ($0.13 – 254 * 10^{-12}$ m^2/s). A closer look at the data reveals several differences in terms of testing techniques (gravimetric, psychrometry, etc), mixture composition (asphalt mastic, asphalt mixture, mixture design), moisture concentration (15% RH, 85% RH, 100% RH), and specimen geometry (thickness to diameter ratio – 1 to 30 mm), and duration of test (approx. 1 to 21 months); which may account for the perceived differences. Another possible source of the apparent discrepancies in the reported diffusion coefficient could be the theoretical models used to estimate diffusion coefficient from moisture uptake data. Most of these studies assume Fickian diffusion can adequately characterize moisture transport in asphalt mixtures. However, some of the basic assumptions of Fickian diffusion such as homogeneity of the diffusing medium might not be completely satisfied in asphalt mastics.

The objective of this study was to examine certain aspects of the experimental conditions (sample geometry, relative humidity, and temperature) and physical properties (mastic constituents and mastic microstructural changes with time) on moisture diffusion in asphalt mastics by applying three different moisture diffusion theories – one Fickian and two non-Fickian (anomalous) models to moisture uptake data. An automated (temperature and relative humidity) environmental chamber was used to obtain moisture uptake data for four nominally similar (except for aggregate and mineral filler type) mastic specimens. The moisture uptake data was fitted to the three aforementioned moisture diffusion models to determine diffusion coefficient and other moisture transport parameters that were in turn used in combination with X-ray computed tomography (X-ray CT) imaging data to suggest some possible explanations for the apparent discrepancies observed in some previous studies. Moisture diffusion in asphalt mastics was related to specimen geometry (thickness), phase of the diffused moisture (bound or free), and time-variable diffusion. Suggestions for the selection of moisture diffusion coefficient for modeling moisture transport in asphalt mixtures were presented.

Moisture Diffusion Models

Fickian Diffusion Model

The first moisture diffusion model studied, the Fickian model, is a two-parameter (equilibrium moisture uptake, M_∞ and diffusion coefficient, D) model as shown in Eq. 1 (Crank, 1975). As the name suggests, the basis for this model is Fick's law which assumes that a) moisture concentration gradient is the potential for mass transfer through a unit area of a section of a material, b) moisture diffusion follows a single free phase absorption model in which the water molecules are not combined with the absorbing material, and c) diffusion occurs in a single direction perpendicular to the plane of the absorbing material. The later assumption is ensured during experimental determination of diffusion coefficient by the use of specimens with very large diameter to thickness ratios. For asphalt mastics diameter to thickness ratios from 5 to 30 have been used (Kringos et al. 2008, Apeagyei et al. 2013). A further consideration of the Fickian model is that molecular diffusion is the only means of moisture absorption in a material. Another assumption of Fickian diffusion is that the material absorbing the moisture is homogenous. For materials and testing conditions satisfying the aforementioned conditions, diffusion coefficient could be considered a material property that is independent of specimen size.

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} e^{\frac{-D(2n+1)^2 \pi^2 t}{l^2}} \quad (1)$$

where M_t is the amount of moisture absorbed at time t, n is an integer, M_∞ is the equilibrium moisture uptake (moisture content at thermodynamic equilibrium), D is the diffusion coefficient and l is the sample thickness.

Langmuir-type Diffusion Model

The second moisture diffusion model studied is the two-phase moisture Langmuir-type diffusion model (Carter and Kibler, 1978) shown in Eq. 2 (Bonniau and Bunsell, 1981). The model is a modification of the Fickian assumption of a single free phase absorption model and thus contains the two parameters (M_∞ and D) in the Fickian model as well as two probability parameters related to the molecular phase of the absorbed water molecules. In this case, it is assumed that the absorbed water molecules exist in two phases - free phase and bound phase. Diffusion of the free-phase water molecules follows Fick's law with concentration dependent diffusion coefficient. However, the free phase water molecules can become bound with a probability of β per unit time. The model further assumes that water molecules can leave the bound state with a probability of α per unit time (Eq. 2). This model was selected because it has been successfully used to investigate moisture in certain polymers that do not completely follow Fick's law (Carter and Kibler, 1978, Bonniau and Bunsell, 1981).

$$\frac{M_t}{M_\infty} = 1 - \frac{\beta}{(\beta+\alpha)} e^{-\alpha t} - \frac{\alpha}{(\beta+\alpha)} \frac{8}{\pi^2} e^{\frac{-D\pi^2 t}{l^2}} \quad (2)$$

Time-Variable Diffusion Model

The final diffusion model considered in this study to examine moisture diffusion in asphalt mastics was a time-variable diffusion model (Weitsman, 1976) which assumes

moisture diffusion is a function of three parameters - the equilibrium moisture content, an initial diffusion coefficient and a constant that describes the rate of change of diffusion with time (Eq. 3). Similar to the Langmuir-type model, this model is a modification of the Fick's model in which the physical time t is replaced with an equivalent t* defined to so as to be a function of the rate of change of diffusion coefficient with time (Eq. 4). The model considers the time dependent physical changes such as physical ageing, curing and stress relaxation commonly associated with polymers and other viscoelastic materials of which asphalt mastics could be considered as one. By substituting Eq.3 and Eq. 4 into Eq. 1 yields the time variable diffusion model as shown in Eq. 5.

$$D = D_0 e^{-\lambda t} \tag{3}$$

where,
D_0 is the initial diffusion coefficient, and λ is the rate of change in diffusion coefficient with time.

$$t^* = \frac{1 - e^{-\lambda t}}{\lambda} \tag{4}$$

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} e^{\frac{-D_0 (2n+1)^2 \pi^2 t}{l^2}^*} \tag{5}$$

Moisture Uptake Profiles

A moisture uptake profile describes the relationship between the amount of moisture (M_t) a hygroscopic material exchanges (absorbs or desorbs), at a given relative humidity and temperature, with time. If w_0 is the initial (dry) mass of a given material and w_t is the mass after time t, then the moisture uptake can be computed as the ratio of the amount of moisture absorbed at a given time to the initial dry mass of the sample at the beginning the test (Eq. 6).

$$Mass\,uptake(\%) = M_t = \frac{w_t - w_0}{w_0} * 100 \tag{6}$$

For a material at a given temperature and relative humidity, moisture uptake increases until it reaches a thermodynamic equilibrium at which point no further changes in moisture uptake occurs. The moisture content at thermodynamic equilibrium (M_∞) is called equilibrium moisture uptake.

Determination of diffusion model parameters

The three selected diffusion models were solved numerically using the Generalized Reduced Gradient (GRG) non-linear regression routine in EXCEL. The predicted moisture sorptions were compared with the laboratory measured data.

Materials and Methods

Materials

Mastic components

Limestone and granite aggregates were obtained from UK quarries. Previous studies (Airey et al., 2007) suggest these aggregates have significantly different susceptibility to moisture-induced damage under laboratory conditions. Therefore, it was expected that mastics made from the selected aggregates would show different sorption and diffusion characteristics. The aggregates were mechanically sieved in the laboratory to obtain only materials passing the 1-mm sieve and retained on 0.125-mm sieve (fine aggregate). In addition to the fine aggregates, limestone and granite mineral fillers satisfying BS EN 1097-7-2008 were used. Again, the choice of the mineral fillers was made to quantify the effect, if any, of different types of fillers used in asphalt mixtures. A 40/60 pen grade from a single source was used for preparing all the mastics.

Mastic Mix Design

The proportion of the constituent components (fine aggregate, mineral filler, bitumen) of the mastics used was 50:25:25 by weight of mixture and was chosen to mimic mastic mix design typically used in open-graded asphalt mixtures in the Netherlands. The aggregate components were weighed separately, combined and thoroughly mixed in a mixing bucket, and heated at the mixing temperature of 185°C for about 10 minutes before adding hot bitumen (185°C) to the mixture. The mixture was mixed using a Hobart mechanical mixer for about five minutes to produce homogenous mastic samples. The mastics were put in quart tins and stored in temperature controlled (20°C, 50% RH) conditions until testing.

Sorption Specimens

Cylindrical disk specimens with nominal diameters of about 25 mm, used for evaluating the sorption and diffusion characteristics of the mastics, were prepared by pouring molten mastic into specially designed silicone molds. The specimens were cooled to room temperature and stored in a desiccator (to keep dry) until testing. The thickness of the specimens ranged from about 2.18 mm to about 4.66 mm. The dimensions used in this study encompassed those used in previous studies. Specimen weight ranged from 1.83 to 3.98 g and averaged about 3.15 g.

Methods

Kinetic Vapor Sorption Profiles

Kinetic vapor sorption profiles for asphalt mastic were obtained using a dynamic moisture vapor gravimetric sorption technique in which an environmental chamber precisely generated and maintained 85% RH at a temperature of 23°C. A TAS Model 600FS LTCL Series 3 environmental chamber capable of maintaining temperatures ranging from -75°C to 180°C and relative humidity from 0 to 95% was used. Air flow in the chamber was estimated to be about 0.50 m/s (about 0.10 m/s near the specimen). The weight gain (moisture uptake) of the mastic specimens was measured periodically (daily) using a Precisa XR 305A balance (Precision Balance Services Ltd) with a 0.1µg resolution. The moisture uptake was monitored until 'thermodynamic equilibrium' (i.e. a change of 0.0001g over a 24 hour period). At least three mastic specimens of each mix type were tested.

X-ray computed tomography

X-ray computed tomography (X-ray CT) is a non-destructive technique for visualizing the internal microstructure of a material based on its X-ray absorption properties. X-ray absorption is related mainly to a material's thickness and density. A typical X-ray CT system consists of a movable X-ray source that sends out a beam of ionizing radiation through a collimator to an array of detectors positioned behind the material being studied. The ratio between the amount of X-ray sensed by the detector array to the original X-ray from the source before it passes through the material gives a measure of the X-ray absorption properties of the material which is then used to generate a 2-D image of a thin projected 'slice' of the material (CT scan). The pixel intensities of a CT scan is related to the X-ray absorption properties of the material which, as previously stated, depends mainly on thickness and density. In general, the denser a material, the brighter the pixel intensity of its CT scan. For example, for a 16-bit grayscale image, a range of pixel intensities from 0 (pure black) to 65535 (pure white) is assigned.

Asphalt mastic samples about 60 mm thick placed inside 87-mm diameter steel cans were tested in two conditions: a) two-day storage at 20°C after mastic manufacture, and b) four-week storage at 20°C after mastic manufacture. These two storage conditions were selected to simulate the microstructural state of a mastic sample at the beginning and at the end of a diffusion coefficient experiment which could last for over three weeks for the current study. A VENLO H-350/225 scanner (X-Tek Industries, Tring, Hertfordshire, U.K.) with two micro-focal X-ray sources (225 and 350 kV), 1829 μA X-ray intensity (640 W power), and 1-mm collimation (slice thickness) was used to scan the asphalt mastic samples at a resolution of 0.083 mm/pixel. Slices were taken at 1 mm intervals along the height of the specimen resulting in over 50 slices per sample.

The resulting 2D images were analysed using ImageJ software to determine the percent of aggregates for each slice and to generate 3-D images of the asphalt mastics. To determine the percentage of aggregates per slide, the images were thresholded by converting representative grey scale of a component into a pixel value (0 to 65536 for 16-bit image) which was then used to identify that component in the mixture. For this study, the threshold values of 0 to 8738 were assigned to the air voids, 8738 to 22102 to the bitumen and 22102 to 65536 to the aggregates. These were arbitrary chosen based on previous studies (Khan et al. 2013).

Results and Discussion

Moisture Uptake Profiles

Moisture uptake profiles were computed as the ratio of moisture uptake at a given time to the original weight (dry weight) of the sample at the beginning of the test (Eq. 6). The dry weight of the mastics tested was 3.15±0.70g. Sample moisture uptake profiles are presented in Figure 1 for the four mastic types considered. The results show differences in moisture uptake based on aggregate and/or filler type. Mastic containing granite aggregate (GA) and / or granite filler (GF) exhibited moisture uptake profiles that plotted higher than those containing limestone aggregates. Also, the results suggest moisture uptake by mastic samples containing granite are higher compared to limestone mixtures in most cases. This latter assertion is clearly demonstrated in Fig. 2 where mastics containing granitic materials [granite aggregate (GA) and granite filler (GF)] show greater equilibrium moisture uptake compared to limestone mastics.

It can also be seen from Fig. 2 that asphalt mastic moisture uptake is influenced by specimen thickness. The effect of thickness on equilibrium moisture uptake appears to be in agreement with Eq. 1 which suggests that for materials following Fickian diffusion, the equilibration time is proportional to the sample thickness squared. Therefore, doubling the thickness should increase the time to equilibration by a factor of 4. This is illustrated in Figure 3 where moisture uptake data for three samples of the mastic

containing LA and LF of different thickness values are compared. For example, moisture uptake for the 2.18-mm specimen after 51 hours (=0.049%) should be equivalent to moisture uptake of the 3.86-mm specimen after 160 hours [$(3.86/2.181)^2$*51] (=0.0.065%), and to the 4.07-mm specimen after 179 hours (= 0.048%). Moisture uptake after 51 hours in the 2.18-mm specimen is equivalent to that for the 4.07-mm specimen after 179 hours which appears to be in accordance with the assumption of Fickian diffusion. The results suggest that for the three mastics under consideration, the 3.86-mm specimen should have been conditioned for 762 days while the 4.07-mm specimen should have been conditioned for 847 days to achieve the same level of moisture as the 2.18-mm specimen conditioned for 243 days. The results suggest thickness is an important factor to consider during laboratory determination of moisture diffusion coefficient for asphalt binders. The results also suggest that the accuracy in the prediction of moisture diffusion in mastics could be improved if a realistic mastic geometry (thickness) is used in the laboratory determination of diffusion coefficient. Currently there are no standard methods for determining mastic thickness in asphalt mixtures.

Diffusion coefficient using Fick's model

Table 2 lists the Fick's model parameters D and M_∞ obtained for moisture diffusion in asphalt mastics. The moisture diffusion coefficients were computed using Eq. 1. Also listed in Table 2 are the coefficient of determination (R^2) values which suggests the Fick's model describes moisture diffusion in mastics quite well. The numerically computed M∞ was comparable to the experimentally determined ones (Fig. 2). The results show that diffusion coefficient vary with thickness. As previously discussed under the moisture uptake section, Eq. 1 suggests moisture uptake is proportional to specimen thickness squared. The same analogy used in Eq. 1 could be extended to illustrate the variation of diffusion coefficient with thickness. Thus, thinner specimens should be expected to reach equilibrium moisture faster than thicker specimens and therefore the diffusion coefficient determined for thinner specimens should be more accurate than for thicker ones. It must be noted that the top aggregate size for the mastic used in this study was 1.0 mm. Therefore, specimen size of 1-mm thick as used in some previous studies might not be representative enough of the bulk mastic. As previously indicated, currently no standards for estimating mastic thickness in an actual asphalt mixture exist. Neither is a universally agreed mastic film thickness in asphalt mixtures. Based on the current study, moisture diffusion appears to be thickness dependent, therefore, there is the need to accurately estimate mastic film thickness in actual asphalt mixtures in order to realistically measure moisture diffusion in mastic.

Diffusion coefficient using Langmuir-type model

Table 3 lists the calculated values for the Langmuir-type model parameters D_L, β, γ and M_∞. Also listed in Table 3 is the coefficient of determination (R^2) values, higher R^2 suggests better model predictions. It is clear from the data ($R^2 > 0.9$) that the Langmuir model is useful for describing moisture diffusion in asphalt mastics.

Equilibrium moisture uptake M_∞ obtained for the Langmuir model was comparatively lower than that obtained for the Fick's model. This could be attributed to the assumption in the Langmuir model that part of the diffusing water molecules are bound to the mastic and therefore do not contribute to moisture uptake due to Fickian diffusion.

From Table 3, for majority of the mixtures, D_L increases with specimen thickness which is similar to the trends observed for the Fick's model. However, D_L appears to be comparatively smaller than the D computed using the Fickian model. This could be attributed to the fact that the Langmuir model considers the absorbed water molecules to be in two phases with one phase governed by Fickian diffusion and the other phase independent of Fickian diffusion (bound and free phases). However, both the Fickian and Langmuir-type models diffusion coefficient parameters were of the same order of

magnitude and followed similar trends with thickness for the majority of the mastics tested.

In contrast to D_L, the two Langmuir model parameters β and γ do not appear to show a clear trend of increasing diffusivity with specimen thickness. What is clear is the fact that β appears to be significantly larger than γ irrespective of mastic type or specimen thickness. This is illustrated in Fig. 4 where the two model parameters are plotted against specimen thickness for the four mastics considered. In all cases, the β-parameter, which represents the probability per unit time of the absorbed water molecules moving from the free to the bound phase was greater (up to four times more) than the γ-parameter representing the probability of water molecules leaving the bound to the free phase. Thus it seems more likely for a portion of diffusing moisture that has bonded to the asphalt mastic, to remain bound within the mastic than to leave the bound state and diffuse freely.

As can be seen in Fig. 4, the probability parameters (β and γ) do not appear to change much for the different (in terms of filler and fine aggregate types). This would suggest the bitumen phase might be the main factor controlling whether water molecules in the mastic remain in the free phase or bound. This later assertion appears more reasonable since for most organic polymers (of which bitumen could be considered one), water molecules could attach readily to their hydrogen or other hydrophilic sites.

It can also be seen in Fig. 4 that the dual phase probability parameters β and γ do not vary significantly for the different mastic types considered in this study and averaged respectively, $6.81 \pm 0.99 \times 10^{-4}$ s^{-1} and $2.18 \pm 0.28 \times 10^{-4}$ s^{-1}. Therefore, it is possible to compute the proportion of total water molecules in the free phase that move from the free phase to the bound phase for the mastics tested as 0.8 [=6.81/(6.81+2.18)], approximately.

Time-variable diffusion

The reason for considering the time variable model for moisture diffusion in asphalt mastic is based on the observation that during a moisture sorption test, the rate of moisture uptake appears to increase rapidly during the initial stages before slowing down considerably during the latter stages of the test (see for example Fig. 1). This behavior is not completely understood but two factors could be used to partially explain it. First, moisture diffusion is assumed to be concentration dependent – the higher the moisture content of a material, the lower diffusion coefficient. Another possible reason, and the one which would be explored further in this paper, is the changes in the material's physical properties (microstructure, ageing, relaxation, etc) with time during the sorption test. Both of these reasons suggest a time variable diffusion coefficient could help explain some aspects of moisture diffusion in mastics.

Table 4 lists the calculated values for the time-variable diffusion model parameters D_o, λ and M_∞ using Eq. 5. From Table 4, it can be concluded that the time-variable diffusion model can be used to describe moisture diffusion in asphalt mastic quite well ($R^2 > 0.9$) Diffusion coefficient D_0 obtained from the time-variable model were found to increase with specimen thickness. Also, D_0 was found to be comparatively higher in asphalt mastic that contained limestone than those containing granite aggregates. Thus, moisture diffusion predictions from the time-variable model are similar to the Fickian and Langmuir model predictions.

A basic premise for the time-variable diffusion model is that because of the physical changes that occur in a polymer, diffusion coefficient decreases with time in proportion to its current value. For the materials tested, rate of diffusivity with time was lower in the mastics that contained either 100% granitic materials (GA + GF) or 100% limestone materials (LA + LF) than in mastics containing a mixture of granitic and limestone materials. Similar trends were seen when the rate of change in diffusion coefficient with time is compared (Fig. 5). In general, for the four mastics studied diffusion coefficient decreased by 3.5, 5.3, 5.5, and 1.7, respectively for mastics LA+LF, LA+GF, GA+LF, and GA+GF. Similar to both the Fick's and Langmuir models, diffusion coefficient predicted by the time-variable model is greater in magnitude in the

limestone mastics compared with the granite mastics. The results suggest that though the time-variable diffusion model can be considered as a phenomenological model and, therefore, has limited interpretative value, it is useful in describing the experimental data quite well.

Characteristic diffusion time

In addition to M_∞, which is obtained after a long conditioning time (equilibrium time) and represents a materials affinity for water, another parameter that can be used to characterize moisture diffusion in a material is the characteristic diffusion time, t_{cr}, which quantifies the duration of the transient portion of the moisture uptake curve. The characteristic diffusion time is defined as the ratio of specimen thickness squared to five times the diffusion coefficient. Table 5 shows the t_{cr} results obtained. It can be seen that diffusion time ranged from an average low of about 8 days for the granite-aggregate granite-filler mastic to a high of 12 days for the mastic containing granite aggregate and granite filler. The results suggest the mastic 'LA + GF' had characteristic time that was comparatively lower than the other three mixtures. Based on the narrow range of values of characteristic time obtained for the various mastics, it can be concluded that mastic characteristic time can be averaged as about 10±1.6 days for mastic thickness of 3.60±0.8 mm. This suggests that during a multi-week sorption test such as the ones conducted in this study, the rate of moisture uptake is greatest during the first 10 days of testing on average.

Asphalt mastic microstructure using X-ray CT

As previously discussed, moisture diffusion coefficient obtained in this study for asphalt mastic varied with specimen thickness. The results were unexpected as diffusion coefficient of a homogenous material is considered a material property and, therefore, is expected to be specimen-size independent. One hypothesis was that asphalt mastic, at the testing conditions considered in this study (23°C), could be considered as a suspension of aggregates (fine aggregate and mineral filler) in a viscous solid (bitumen) and therefore Stoke's and Newton's drag laws may apply. In this case the aggregate fraction of the mastic could settle due to gravity and the viscoelastic nature of the bitumen resulting in a graded material with the bulk of the more dense aggregates settling to the bottom and the lighter filler and bitumen remaining near the top. Should this situation occur, then the mastic could not be considered homogenous and therefore may not exhibit thickness independent diffusivity as assumed under Fick's law. To test the hypothesis, the technique of X-ray CT was applied to study the microstructure of asphalt mastic in order to quantify the degree of homogeneity (settlement of aggregates) of the material. A review of the literature found no previously published study on the effect of specimen geometry on moisture diffusion in asphalt mastics and on the use of X-ray CT technique to better understand microstructural changes over time in asphalt mastics.

The time required to complete a typical diffusion test on asphalt mastic is on the order of hundreds of hours (equivalent to several weeks). In an attempt to capture the asphalt mastic microstructural changes over a similar time scale, X-ray CT scans were made immediately after mixing the mastic (2-days of storage at 20°C) and also after four weeks of storage (to simulate the length of a typical diffusion test). For mastic samples at each testing condition (2-days and 4-weeks), about 50 X-ray CT scans, taken at a spacing of 1-mm scanning interval, were obtained for analysis. The image analysis software, ImageJ was used for all the analyses. The objective of the analyses was to quantify the amount of fine aggregates of a given size or pixel intensity range (grayscale) in each 1 mm thickness of the mastic. To accomplish this objective, the X-ray CT images were segmented to obtain the different phases (air voids, bitumen, mineral filler, and fine aggregates) of the asphalt mastic by performing threshold analysis using the ImageJ software. By assigning carefully selected grayscale values ranging from 0 to 65536 (threshold analysis), the distinctive grayscale intensities in the output image enabled a

distinction between the various components of the mastic to be made. First, arbitrary threshold grayscale ranging from 0 to 8738 levels were assigned to air voids, 8738 - 22102 to the bitumen, and 22102 to 65536 to the aggregates. The number of particles with a specified area and grayscale were counted automatically to estimate the percent aggregate in a layer.

Fig. 6 shows a comparison of a segmented X-ray CT scan images for the top 2 mm and the bottom 2 mm of asphalt mastic sample stored at room temperature for a month. In Fig. 6, white particles represent aggregate particles while black particles represent bitumen. As could be seen in Fig. 6, more fine aggregates (whiter and larger particles) appear near the bottom 2mm than the top 2mm. Fig. 6 demonstrates that the internal structure of the mastic near the bottom of the mastic can be significantly different from the material near the top which suggests material inhomogeneity for asphalt mastic stored at room temperature for about four weeks.

Following the threshold analysis, the aggregate particle size distribution with depth was estimated by counting the number of particles satisfying the grayscale criteria described previously. The results are presented in Fig. 7 where the percentage of aggregate of the specified pixel intensity and size are plotted against mastic specimen thickness. The results showed significant settlement of the denser aggregate particles with depth for the four-week old mastic with the percentage of aggregates satisfying the specified criteria ranging from 15% near the bottom to almost zero near the top. The effect was especially significant near the bottom one-third of the specimen. On the contrary, for the 2-day old mastic, the amount of aggregate satisfying the threshold criteria remained consistent at about 12% throughout the material. The data suggest a significant density/material gradient occurs in asphalt mastic with time at room temperature which could partially account for the apparent variation of thickness with diffusivity of asphalt mastic observed in this study. Thus the homogeneity of the mastic samples cannot be assumed during diffusion testing of mastics. Since the extent to which solid material will settle in a viscous material depends on the solids grain size, shape, and density; different aggregates will settle differently in a given type of bitumen. Therefore, the change in microstructure with time is an important property of asphalt mastics that should be characterized when studying moisture diffusion in asphalt mastic.

Factors influencing diffusion coefficient of asphalt mastics - Discussion

One objective of this study was to identify factors that influence moisture diffusion in asphalt mastics in order to better understand moisture damage in asphalt mixtures. Several factors were considered including aggregate type, mineral filler type and specimen thickness. The importance of the first two factors (aggregate type and filler type) on moisture diffusion is obvious even though their effect on the actual mechanism of moisture damage is not clear. The third factor was important to consider because the diffusion coefficient determined in this study is expected to be used as input for numerical simulation of moisture damage in asphalt pavements and therefore any thickness effect (anisotropy), if any, needs to be documented. It is generally assumed that diffusion coefficient is an intrinsic material property that is independent of thickness but this has not been verified for asphalt mastics in previous studies. One assumption of Fickian diffusion is that diffusion occurs in homogenous materials. X-ray CT scan data of selected asphalt mastic considered in this study suggest significant settlement of the denser fine aggregate near the bottom of an asphalt mastic specimen can occur over the time frame that is equivalent to the typical duration of the gravimetric moisture sorption test for determining moisture diffusion coefficient. Thus, assumption of a homogenous material may need to be qualified when considering laboratory determination of asphalt mastic moisture diffusion.

The results of the current study showing significant material gradient support the two dimensional diffusion in asphalt mastic suggested in a previous study (Apeagyei et al. 2013). The diffusion coefficient (based on Fick's law) values reported in this paper ranged from 0.9 to 5.3 x 10^{-12} m^2/s depending on thickness and aggregate type. This

compares with the reported moisture diffusion coefficient of certain aggregates (granite and sandstone) of 120-200 x 10^{-12} m^2/s (Kringos et al 2008) and of certain dolomite of 80800 x 10^{-12} m^2/s (Henon et al. 2002) suggesting moisture diffusion in uncoated aggregates several orders of magnitude higher than in asphalt mastic. Tests conducted on bitumen of similar penetration grade as that tested in this study showed diffusivity in pure bitumen was lower but of the same order of magnitude as the mastics. Given that moisture diffusion in air (2.6 million mm^2/s) is more than seven orders of magnitude higher than in mastics, the effect of thickness on moisture diffusion in asphalt mastic could be attributed in part to settlement of aggregate (possibly creating some air pockets as they settle) and to the differences in the magnitude of aggregate diffusivity and that of the mastic.

Summary and Conclusions

The objective of this study was to investigate certain aspects of asphalt mastic moisture diffusion characteristics in order to better understand the moisture damage phenomenon in asphalt mixtures. Gravimetric moisture sorption experiments were conducted using an automated environmental chamber on four different asphalt mastics containing granite and limestone aggregates. X-ray CT techniques were applied to characterize the microstructure of the asphalt mastics in order to quantify the degree of inhomogeneity. Fickian and two non-Fickian models including the two-phase Langmuir-type model and a two-parameter time-variable model were all were found to describe the experimental moisture diffusion data quite well (R^2=0.9). Moisture diffusion was found to be influenced by aggregate type and specimen thickness, which was unexpected. The observed variation of diffusion coefficient with thickness was attributed in part to microstructural changes (settlement of the denser fine aggregates near the bottom of the material) during the rather long-duration diffusion testing. This assertion was supported by X-ray CT imaging of the mastic that showed significant accumulation of larger fine aggregate particles near the bottom of the sample with time. The results from the Langmuir-type model supported a two-phase (free and bound) model for moisture absorbed by asphalt mastic and suggests about 80% of absorbed water in the free phase remain bounded within the mastic. The results also suggested that moisture diffusion in asphalt mastic may be time-dependent with diffusion decreasing by more than four times over the initial diffusion during a typical diffusion test lasting up to 500 hours. The study concludes that both geometry and time-dependent physical characteristics of mastic are important factors to consider with respect to moisture diffusion in asphalt mastics. Future studies should characterize the microstructural changes that can occur within the time scale of a typical sorption test in an attempt to better understand the moisture damage phenomenon in asphalt mixtures.

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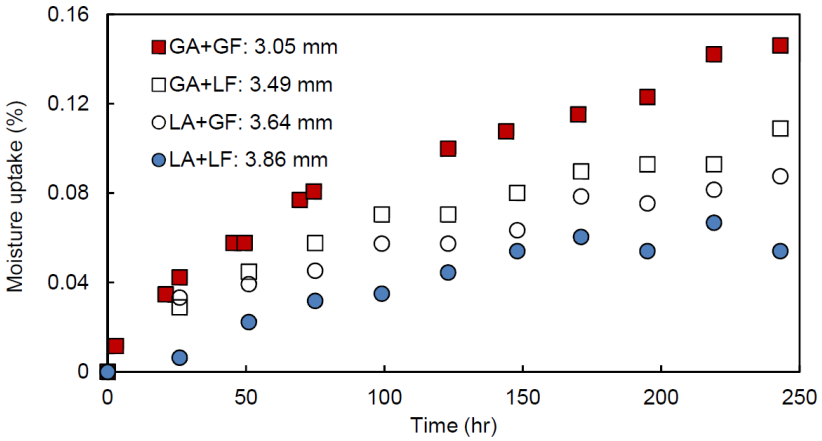

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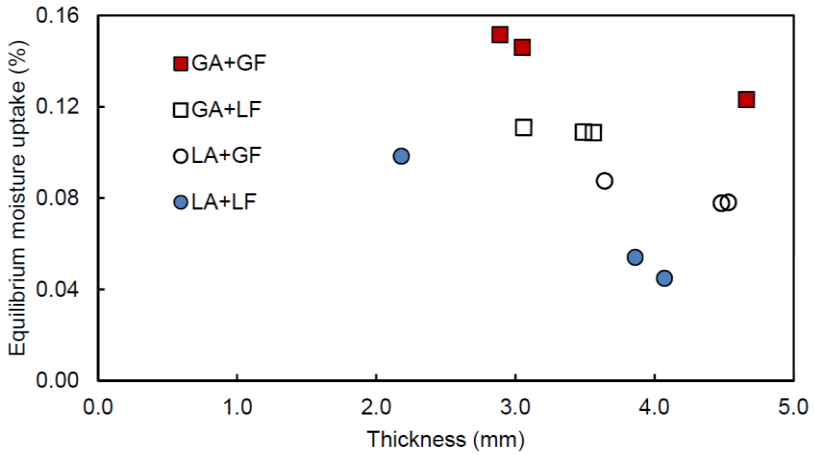

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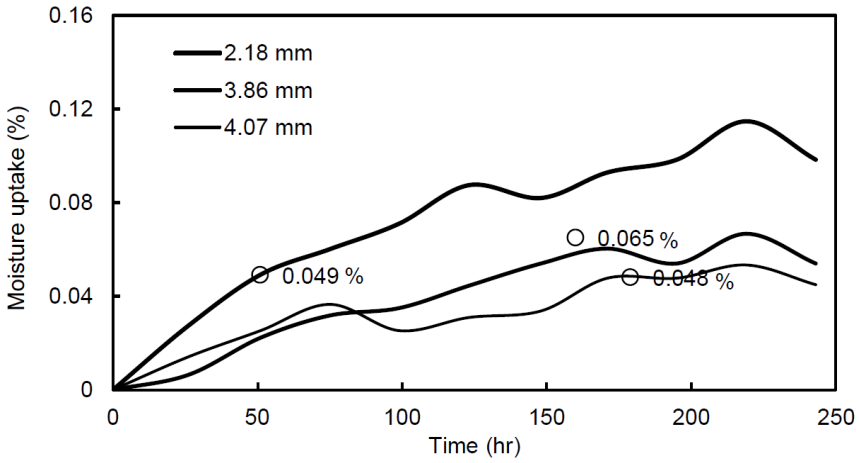

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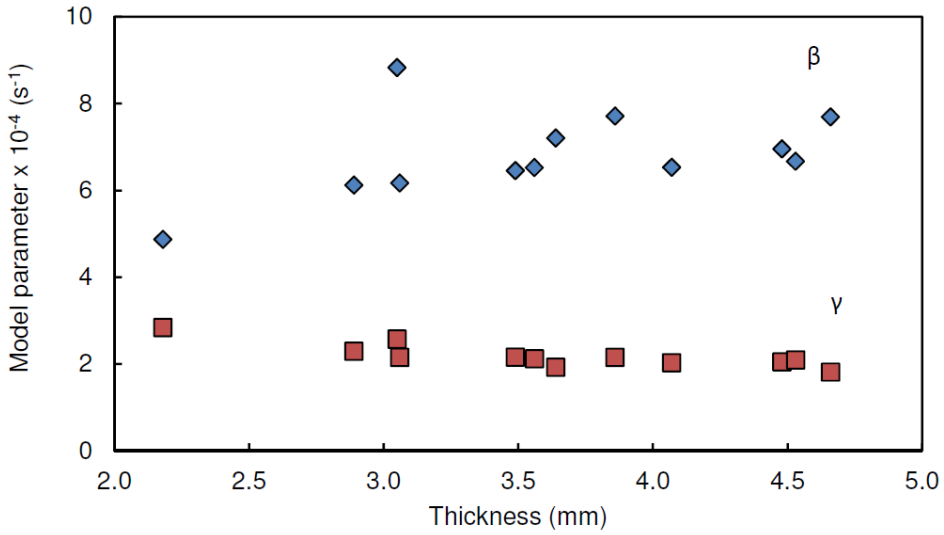

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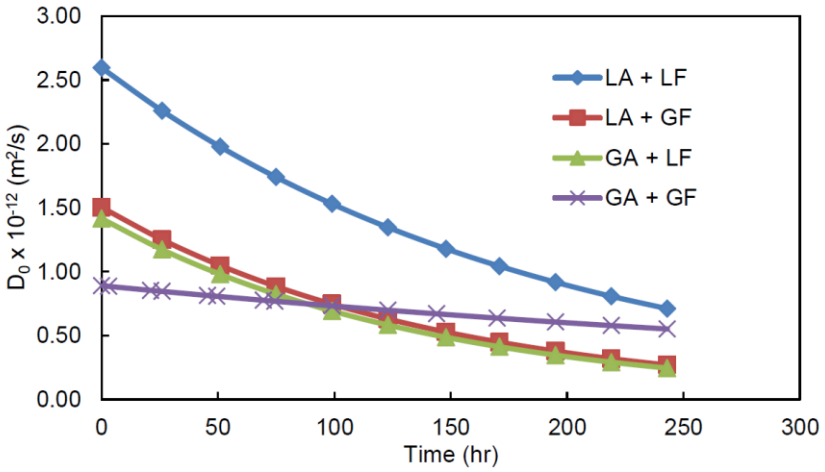

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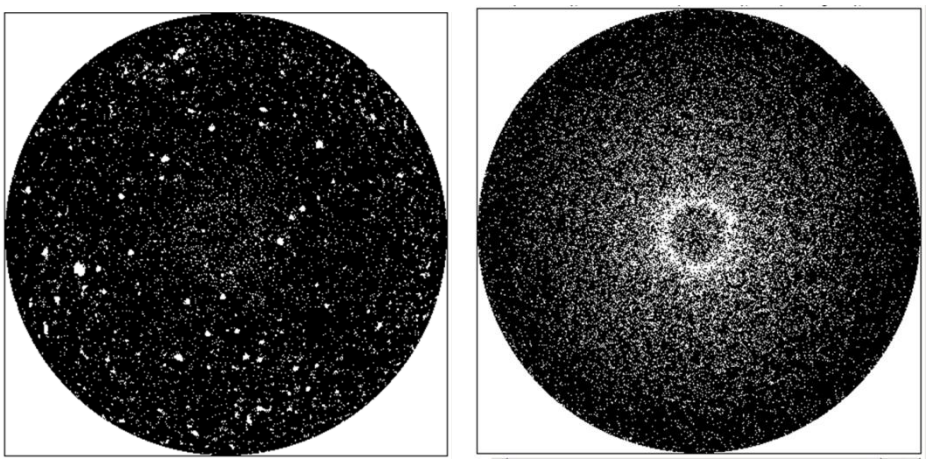

(a) (b)

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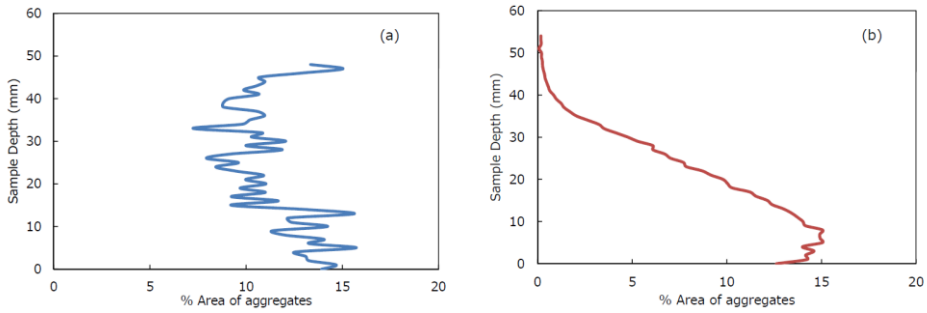

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Table 1 Sample reported asphalt mastic diffusion coefficients

Reference	Blend proportions (by weight)	D x 10^{-12} (m^2/s)	Specimen characteristics and experimental conditions
Kassem et al. (2006)	Aggregate: 52.4% sandstone, 35.0% igneous screening, 4.6% hydrated lime asphalt: 8.0% PG 76-22	10.3	Cylindrical specimens, 50 mm in diameter and 50 mm in height, sitting in a shallow water bath at 25°C, while measuring the change in the logarithm of total suction using a psychrometer embedded in the middle specimen and placed 5 mm above the bottom end of the of the specimen. Aggregate size passing sieve Number 16 (1.18mm). Air voids not specified.
	Aggregate: 66.2% natural sand, 25.8% limestone sand asphalt: 8.0% (PG 64-22 & PG 64-28)	9.72 & 24.3	
Kringos et al. 2008	Aggregate: 50% crushed sand, 25% lime asphalt: 25% binder (Pen 70/100, Cariphalt XS, Sealoflex)	0.13 - 0.36	Gravimetric sorption method applied to 30 mm × 30 mm and 1 mm thick specimens placed inside an 85% relative humidity chamber at 25°C. Aggregate size (top size 1.18 mm). Air voids not specified.
Arambula et al. (2010)	Aggregate: 47.3% diabase, 42.5% sand, 1.7% dust asphalt: 8.5% PG 70-22	254.0	Gravimetric method (ASTM E96, wet cup/dry cup method) applied to cylindrical ensembles containing 70 mm diameter and 4–5 mm thick specimens, where the ensembles were placed in a chamber with 15% relative humidity at 35°C. Aggregate size passing sieve Number 4. Air voids between 11–13%. Used Fick's first law to estimate D.
Vasconcelos et al. (2011)	Aggregate: N/A, asphalt: 8.9% (PG 58-XX, XX=10, 22, 28)	20.4 & 11.7	23.9 °C temp. Conditioning by submerging in water for 21 months and measuring SSD with time using a sensitive mass balance. Aggregate size passing sieve 1.18 mm sieve. Air voids between 7–11%.
	Aggregate: N/A asphalt: 8.9% (PG 58-XX, XX=10, 22, 28)	41.9 & 26.9	37.8 °C temp. Conditioning by submerging in water for 14 months and measuring SSD with time using a sensitive mass balance. Aggregate size passing sieve 1.18 mm sieve. Air voids between 7–11%.

Table 2 Fick's model parameters for moisture diffusion in asphalt mastics

[1]Mix ID	Thickness (mm)	M_∞ (%)	D x 10^{-12} (m^2/s)	R^2
LA + LF	2.18	0.115	1.1050	0.973
	3.86	0.078	2.1770	0.936
	4.07	0.066	2.2320	0.887
LA + GF	3.34	0.088	3.3500	0.967
	4.48	0.079	5.1970	0.970
	4.53	0.082	5.3420	0.961
GA + LF	3.06	0.118	2.0280	0.978
	3.49	0.115	2.4360	0.987
	3.56	0.123	2.5930	0.992
GA + GF	2.89	0.216	0.8790	0.985
	3.05	0.207	0.9830	0.982
	4.66	0.167	1.8360	0.992

[1] LA = limestone aggregate; LF = limestone filler; GA = granite aggregate; GF = granite filler.
[2] Diffusion coefficients determined assuming 3-mm thick samples.

Table 3 Langmuir model parameters for moisture diffusion in asphalt mastic

Mix ID	thickness (mm)	M_∞ (%)	D_L (m^2/s) x 10^{-12}	β x 10^{-4} (s^{-1})	γ x 10^{-4} (s^{-1})	R^2
LA + LF	2.18	0.110	2.652	4.87	2.84	0.965
	3.86	0.101	2.074	7.71	2.15	0.916
	4.07	0.080	2.518	6.53	2.03	0.800
LA + GF	3.64	0.117	2.603	7.20	1.92	0.984
	4.48	0.109	3.898	6.95	2.05	0.952
	4.53	0.076	3.507	6.67	2.09	0.794
GA + LF	3.06	0.191	1.269	6.17	2.15	0.976
	3.49	0.165	1.913	6.45	2.16	0.989
	3.56	0.175	2.026	6.52	2.12	0.966
GA + GF	2.89	0.172	1.223	6.12	2.29	0.990
	3.05	0.174	2.196	8.83	2.57	0.977
	4.66	0.173	2.530	7.69	1.81	0.990

Table 4 Time-variable model parameters for moisture diffusion in asphalt mastic

Mix ID	l (mm)	M_∞ (%)	D_0 (m^2/s) x 10^{-12}	λ x 10^{-4} (s^{-1})	R^2
LA + LF	2.18	0.0970	2.594	53.31	0.900
	3.86	0.0780	3.064	49.35	0.909
	4.07	0.0680	3.036	49.79	0.877
LA + GF	3.64	0.1560	1.503	70.71	0.956
	4.48	0.1720	1.677	67.73	0.957
	4.53	0.1630	1.713	67.39	0.963
GA + LF	3.06	0.1740	1.414	72.13	0.952
	3.49	0.1770	1.546	69.92	0.969
	3.56	0.1900	1.618	68.75	0.986
GA + GF	2.89	0.2270	0.890	19.71	0.980
	3.05	0.2230	0.937	19.52	0.977
	4.66	0.1550	2.420	25.02	0.984

l = specimen thickness

Table 5 Characteristic diffusion time for asphalt mastics

Mix ID	l (mm)	D x 10^{-12} (m^2/s)	t_{cr} (days)	Ave	Stdev
LA + LF	2.18	1.088	9.9	10.4	0.6
	3.86	3.065	11.0		
	4.07	3.629	10.4		
LA + GF	3.34	3.252	7.8	8.2	0.4
	4.48	5.287	8.6		
	4.53	5.724	8.1		
GA + LF	3.06	2.327	9.1	9.1	1.0
	3.49	2.726	10.2		
	3.56	3.544	8.1		
GA + GF	2.89	1.700	11.2	11.9	1.3
	3.05	1.906	11.1		
	4.66	3.699	13.3		

l = specimen thickness; t_{cr} = characteristic diffusion time